

MEMBRANE — SOLUTION ION INTERACTION AND ITS EFFECT ON THE PHASE TRANSITION OF
LIPID BILAYER MEMBRANES

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An increase of membrane surface charge density (σ) in general causes lowering of the ordered to fluid state phase transition temperature (T_t) /3/. This is understandable in view of the increased area per lipid molecule in the fluid phase and the tendency of the electrostatic interactions to dilate the membrane area (A). It is the purpose of this paper to estimate the contribution of the lateral compressibility of the two phases of the membrane to the electrostatically induced transition temperature shift (ΔT_t^{el}).

A phenomenological description of the lipid membrane phase transition is invoked /2/. The free energy of the system is described as the sum of the free energy of the corresponding uncharged membrane and the contribution arising from the electrostatic interactions:

$$G(A, T) = G^0(A, T) + G^{el}. \quad (1)$$

The lateral pressure of a lipid bilayer is zero and therefore

$$\partial G(A, T) / \partial A = 0. \quad (2)$$

The free energy of the uncharged membrane at a value of membrane area A close to the value A^0 is written in an expanded form as

$$G^0(A, T) = G^0(A^0, T) + \frac{1}{2A^0\kappa} (A - A^0)^2 \quad (3)$$

where $\kappa = -(\partial A / \partial \pi)_T / A$ is the lateral compressibility coefficient. The electrostatic contribution to the free energy, also written in the expanded form, is

$$G^{el}(A) = G^{el}(A^0) + \pi^{el}(A - A^0) \quad (4)$$

where π^{el} , the effective lateral pressure due to the electrostatic contribution, is at the high surface charge density limit of the Gouy-Chapman approximation (with k the Boltzmann constant and e_0 the unit charge) equal to

$$\pi^{el} = -2kT\sigma/e_0. \quad (5)$$

It is assumed that for the uncharged membrane the phase transition occurs at T_t^0 and that the membrane areas of the ordered and fluid phases are A_1^0 and A_2^0 , respectively. By invoking the equality of free enthalpies of the membrane phases at the transition temperature, T_t^{el} , corresponding to a given value of π^{el} , and retaining linear terms in the expansion of free energy in the temperature shift, $\Delta T_t^{el} = T_t^{el} - T_t^0$, the following expression is obtained for ΔT_t^{el} :

$$\Delta T_t^{el} = [\pi^{el}(A_2^0 - A_1^0)/\Delta S^0] \left[1 - \frac{\pi^{el}}{2} (\kappa_2 A_2^0 - \kappa_1 A_1^0)/(A_2^0 - A_1^0) \right] \quad (6)$$

where the entropy change ΔS^0 is $\partial G^0(A_2^0, T_t^0)/\partial T - \partial G^0(A_1^0, T_t^0)/\partial T$. The expression obtained for ΔT_t^{el} can be trusted only within the validity of the expansion of the free energy function $G(A, T)$. Nevertheless, it can be used to point out that due to the difference in the lateral compressibilities of the two membrane phases the second order of electrostatic contribution may be significant. For the typical values expected for the lipid membranes, $A_1^0 = 0.5 \text{ nm}^2$, $A_2^0 = 0.6 \text{ nm}^2$, $\kappa_1 = 2 \text{ m/N}$, $\kappa_2 = 20 \text{ m/N}$, and $\pi^{el} = -0.016 \text{ N/m}$, obtained by taking $T = 310 \text{ K}$ and $\sigma/e_0 = 1/0.55 \text{ nm}^{-2}$ corresponding to singly ionized lipid molecules, the correction factor to the first order contribution to T_t shift, the latter being $\pi^{el}(A_2^0 - A_1^0)/\Delta S^0 / 3$, has the value 1.9. If the lipid molecules bear two charges, the correction factor is 2.8. These estimates indicate that the electrostatic interaction may at least partly explain the nonlinear increase in the T_t shift which was observed in phosphatidic acids /4/ and phosphatidylserines /1/ when comparing phase transitions of singly and doubly ionized lipid molecules.

References

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